Considerations in the determination of chemical and physical properties as an aid for electrochemical depositions in ionic liquids

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In recent years a large number of articles on electrodeposition of metals from ionic liquids have been published, e.g. reference 1. Along with the popularity of the subject an increased interest in chemical and physical data determined in these media exists[2]. While lists of fundamental data such as diffusion coefficients, formal potentials, nucleation parameters etc. determined in aqueous solutions or molecular solvents are readily available, determinations in ionic liquids are scarce. Moreover, it is not always clear if common procedures used for determinations of such parameters in classic solvents are suitable in combination with ionic liquids.

This study intends to evaluate critically the applicability of electrochemical methods commonly used for determination of fundamental data in classic solvents for use with ionic liquids or ionic liquid analogues. If necessary the methods will be adapted in order to perform optimally in the latter solvents.

The final goal is to collect information on the speciation of metal ions in ionic liquids (or analogues) and its relationship with the electrodeposition of the metal. The electrodeposition of copper in choline-based ionic liquid analogues has been chosen as a reference. The extensive literature available for electrodepositions of copper in aqueous and non-aqueous solutions is a good basis for comparison. Moreover, electrodepositions of copper in ionic liquids show typical features that are specifically attributed to the use of this type of solvents.

Diffusion coefficient

First a thorough evaluation on the determination of diffusion coefficients in ionic liquids will be performed. Both chrono-amperometric and reversed chrono-amperometric experiments are considered to be more reliable methods to determine the diffusion coefficient of an electro-active species than cyclic voltammetry. Based on the work of Von Stackelberg[3] a special cell has been constructed in order to ensure planar diffusion to the electrode surface. Considerations of the use of this cell in ionic liquids are made. Especially, charging current and uncompensated resistance have to be considered with care in these media.

The Stokes-Einstein equation provides a link between viscosity and diffusion coeffient of a species with the equivalent spherical particle size as parameter. This equivalent particle size is an estimate of the size of the metal complex and its surrounding solvatation sphere. In this way it gives an indication of the speciation of the component in solution.

Furthermore, knowledge of the diffusion coefficient of both oxidizing and reducing species enable a more exact determination of the formal standard reduction potential in a particular ionic liquid.

Speciation

Potentiometric titrations are widely used to evaluate equilibrium constants in aqueous solutions. Besides these titrations this study explores the use of conductometry and spectrophotometry to clarify the copper-chloride-ionic liquids complex.

References

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3) M. v. Stackelberg, M. Pilgram, V. Toome, *Z. Elektrochem.* (1953) Volume 57, Issue 5, p 342-350.